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DEGRADATION OF SLUDGES FROM HEAVY CRUDES IN CONTAINED REACTORS

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Prince George Bioreactor For Oily Sludges Degradation
[Part of the Program of the Federal Panel on Energy R&D (PERD)]

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42 pp

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EXECUTIVE SUMMARY

A prototype bioreactor for oil degradation was installed at Husky Oil's Prince George refinery in the fall of 1988. There was an initial rapid increase in the number of oil degrading microbes in the reactor. During the winter months when the temperatures reached extremes the reactor froze. However, the oil degrading microbes remained viable and the following spring, their numbers remained as high as in the previous fall. Oil degradation progressed over the next several months and by late summer/early fall, 1989 71% -77% of the oil had been degraded. Gas chromatography patterns of the recovered oil suggest that lesser amounts of the higher molecular weight alkanes (> C-20) are being degraded in the bottom of the bioreactor. This may indicate oxygen limitations in this area of the reactor. It is suggested that the residual material in the bioreactor be placed on a landfarm plot to determine its fate during landfarming. Options for the bioreactor include running to completion through stimulated biodegradation and cometabolism, assessment for landfilling the matrix and landfarming the matrix containing the residual oil.

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SOMMAIRE

Un réacteur pour la biodégradation du pétrole etait construit a la raffinerie de Husky Oil a Prince George, C.B. en automne de 1989. Les nombres des microbes ont acroissés rapidement dans le réacteur. Pendant l'hiver, le réacteur était congelé à cause de la température fraiche. Cependent, les microbes restent viable et en printemps 1989 les nombres etaient autant elevés qu'en automne. Apres 11 mois 71% -77% du pétrole etait dégradé. La chromatographie gaseuse, a suggére que les molecules plus grand de C-20 sont moins degrades un fond du réacteur. Pour les huiles restants dans le reacteur, il ya des methodes pour stimuler la dégradation. C'est aussi possible a amener les materiaux residuels au terre pour y décider son destin dans un milieu aerobique ou anaerobique.

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1.0 OBJECTIVE

To monitor oil degradation in the contained bioreactor equipped with leachate recycle and located at Husky Oil's Prince George Refinery.

2.0 INTRODUCTION

A field bioreactor containing tank bottom sludges absorbed to Oclansorb heat-treated peat was installed at Husky Oil's Prince George refinery in the fall of 1988. The reactor was in operation over the winter months and self-heated until the extreme temperature froze it. During this time, microbial numbers increased in the reactor and significant levels of oil were degraded (1). During the spring/summer of 1989, the reactor was recharged with fertilizer and allowed to run for the rest of the year. During this interval oil and microbial levels were monitored.

3.0 MATERIALS AND METHODS

3.1 Microbial analysis

Analyses of microbes in the reactors were performed by the most probable number technique. Replicate samples from each sampling time were serially diluted from 10^{-1} to 10^{-12} in tubes of liquid culture medium and incubated for 14 days at ambient temperature. Turbid tubes indicating microbial growth were enumerated. These data were applied to standard probability tables published for this technique to estimate the number of bacteria per gram of compost material or per litre of leachate (2).

Minimal medium for enumeration of oil degrading organisms contained:

$K_2HPO_4.3H_2O$	13.1 g
$NaH_2PO_4.H_2O$	5.75 g
NH_4NO_3	2.0 g
$MgSO_4.7H_2O$	0.315 g
$CaCl_2.2H_2O$	0.0006 g
$FeSO_4.7H_20$	0.001 g
Distilled water	1 L
Final pH = 6.8	

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Complex medium used to test for heterotrophic growth contained:

K_2HPO_4	10.0 g
NaH_2PO_4	5.0 g
NH_4NO_3	2.0 g
$MgSO_4.2H_2O$	0.2 g
$CaCl_2.2H_2O$	0.001 g
$FeSO_4.7H_2O$	0.001 g
Yeast extract	0.4 g
Nutrient broth	0.4 g
Distilled water	1 L

These media were dispensed 4.5 mL per tube. After the tubes were inoculated, 50 microlitres of Amauligak crude oil were added to each tube of minimal medium. Organisms which grew on and degraded the oil turned the tubes turbid and dispersed the oil.

3.2 Water analysis

Water analysis for the presence of polyaromatic hydrocarbons (PAH's) was performed by Core Laboratories, Calgary, Alberta. PAH's were analysed by the EPA 625 method after extraction with dichloromethane from 500 mL water samples. Analysis was on an HP 5890 gas chromatograph and an HP 5970 mass spectrometer.

3.3 Extracted oil

Samples (50 - 100 gram) of Oclansorb/oil matrix were removed from the reactor for oil extraction and analysis. Oil extraction was performed for six hours by the technique of Dean and Stark (Appendix 1) using hot dichloromethane. The extracted oil was rotovaporated to remove the dichloromethane and the residue was weighed. The ratio of extracted oil to extracted oil plus solids was calculated. Comparison of this ratio with that of the original ratio placed in the reactor allowed calculation of the percent oil loss over the period of operation. A sample of the dried extracted oil was dissolved in carbon disulfide and subjected to gas chromatography in order to obtain a characteristic fingerprint of the oil and show how the patterns changed as degradation proceeded.

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Gas chromatography was performed with a Perkin Elmer Sigma 2000 gas chromatograph equipped with an SPB-5 fused silica capillary column (30 m x 0.32 mm ID). The head pressure of the column was 75 kiloPascals and the splitter gas flow was 30 mL/min. The purge gas flow was 3 mL/min. The injector and detector temperature was 320 degrees. The instrument was programmed to run at 70 degrees for ten minutes, then increase the temperature by 10 degrees per minute up to 100 degrees, followed by a 3 degree per minute increase up to 300 degrees. The temperature was maintained at 300 degrees for 30 minutes. The output of the resulting data was on an HP3390A integrator with chart speed set at 0.4 cm/min. A one microlitre sample was use for injection.

4.0 RESULTS AND DISCUSSION

4.1 Microbial numbers

Although the bioreactor froze in January/February 1989, the microbes within it remained viable. After the spring thaw, the microbial numbers in the bioreactor remained high at 10^8 - 10^9 per gram of matrix at eight months operation, similar to levels reported previously (Table 1) (1). There were higher numbers of microbes associated with the matrix than free in the water fraction indicating their concentration in a locality where the oil is present.

Slightly more organisms were present at the bottom layers of the reactor than there were at the top probably indicating more microbial activity in this area of the reactor. As the easily degraded materials in the top of the reactor were used up, the microbes may have migrated to the lower depths to attack these materials here also. The other possibility is that increased microbial numbers in the lower depths are growing, at least partially, on metabolic products leached from the microbes in the upper layers. Lee and Levy demonstrated that increased microbial numbers in the ocean following an oil spill were not degrading oil but were using the metabolic products of organisms killed by the oil spill (9).

4.2 Temperature

The temperature in the reactor was taken twice in the summer. At both times the temperature was 20 - 22 degrees and was not higher than the temperature of the sump. Presumably, the recirculating water in the sump acted as a heat exchange to cool the reactor and maintain the temperature near ambient. This contrasts with observations made during the fall and winter of

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1988 - 1989 when the reactor self-heated to a notable extent against an ambient temperature close to zero (1). However, in its new location at the tank farm during the summer, the bioreactor and the sump were no long covered to prevent heat loss. Presumably, therefore, the sump served as a heat exchanger. Initially, the oil in the reactor consisted of proportionately more of the lighter molecular weight components (< C-20) which are easier to degrade. Increased degradation of these relatively smaller molecules could have resulted in more rapid heat generation. Bench scale reactors degrading Prince George oily sludge in the laboratory consistently ran a few degrees above ambient (3,4).

4.3 Water analysis

Polyaromatic hydrocarbons were not present in the sump above the detection limit of 2 micrograms/litre (Table 2). Volume changes in the water fraction over the course of the study make this an approximate concentration. Concentrations of PAH's in sludges from conventional oil refining are generally in the order of tens to hundreds of milligrams per kilogram (10,11) and solubilities are in the order of 0.004 to 30 mg/L of water (8). Because this sludge consists of primarily waxy residues, the PAH levels are expected to be low. However, PAH's are not believed to be readily degraded and therefore should accumulate. Their absence from the reactor leachate indicates they are being biodegraded. This agrees with observations made in the bioreactor previously (1).

4.4 Hydrocarbon content

Total hydrocarbon content of the bioreactor decreased over the year's operation. At two months operation the oil loss in the reactor was 10.5% at which time the reactor froze due to the extremes of weather. The reactor thawed out in the spring of 1989 and resumed running. After 8 months operation the oil content had decreased to 6.4% - 8.1% indicating 71% - 77% oil loss (Table 3). Gas chromatograms of the oil recovered from the bioreactor indicated extensive degradation/loss of molecules in the C25 -C30 region (Figure 1). The pattern of oil loss from six locations in the reactor indicated less oil loss in the bottom of the reactor than in the top (Figure 1,2). This is unlikely to be due to oil migration from the top to the bottom of the reactor since measurements of oil content from the bottom of the reactor did not indicate any increases in oil concentration in this region compared to samples taken at eight weeks operation. A more plausible explanation is oxygen limitation at the bottom of the bioreactor. Oil degradation is initially an aerobic process. Passive aeration is achieved by the slotted tubes passing through the reactor and by aeration of the recirculating water when it passes through the sump. As water percolates through the reactor,

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oxygen will be removed by the microbes. By the time the recirculating water reaches the bottom of the reactor most of its oxygen has been stripped resulting in decreased oil degradation in this area. Presumedly, this situation will be reversed as the more readily degraded molecules are depleted in the upper layers. Less microbial activity here will reduce oxygen demand and allow more oxygen to reach the lower levels resulting in increased microbial activity and oil degradation there.

A composite sample taken from the reactor at 11 months did not show any great change in oil content (Table 3) or in GC pattern (Figure 3) over those observed at 8 months. This may be due to nutrient limitation in the reactor and/or accumulation of more recalcitrant residual oil as a consequence of biodegradation. It is generally accepted that the progress of microbial degradation of oil usually starts with the smaller and more easily degraded molecules leaving behind the more complex and more difficult to degrade components (5,6,7).

The reactor may have reached a point where microbial growth is self-sustaining but little additional oil degradation is being achieved. Oil degradation could be driven to completion by mixing the oil degrading matrix and refertilization plus adding an additional carbon source to support microbial growth and which would allow the residual oil to be degraded by cometabolism. Many organisms, while growing on one substrate, can attack other substrates which they cannot use to obtain energy for growth. This process is called cometabolism and has been used to initiate microbial attack on many materials including chlorinated hydrocarbons (12).

5.0 CONCLUSIONS

1. Over an 11 month operational period 71% - 78% of oil was lost in the bioreactor at Prince George refinery.

2. Microbes attached to the Oclansorb matrix remained viable after freezing and the reactor restarted in the spring.

3. More oil appeared to have been degraded in the top layers of the reactor than the bottom.

4. Oxygen limitation may have inhibited oil degradation in the bottom of the reactor.

5. Reduced oxygen demand in the upper layers allowing greater oxygen penetration or percolation of metabolic products able to act as nutrients from the upper layers to the lower

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depths of the bioreactor may be responsible for increased microbial numbers in the bottom of the bioreactor at 8 months operation.

6. PAH's did not accumulate in the leachate water and were probably being degraded.

6.0 RECOMMENDATIONS

1. This reactor has been running now for over a year. It should be assessed for volatile hydrocarbons escaping from the matrix and for PAH's in the matrix. It should also be assessed against the EPA leaching criteria (Toxicity Characteristic Leachibility Procedure) for landfilling (Appendix 2).

2. Alternatively, the reactor matrix could be remixed with a pitchfork, refertilized and water flow reversed through the bottom or air forced through the aeration tubes to stimulate the degradation process.

3. Scenarios to promote final degradation could include permanganate treatment, addition of carbon sources to promote cometabolism or increasing the heat in the reactor. However, heating the reactor could impact release of volatiles.

4. The reactor matrix contains a high number of oil degrading microbes. The matrix could be landfarmed in a test plot at Prince George to determine the fate of the residual oil absorbed to the Oclansorb once it has been ploughed into a landfarm.

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8.0 TABLES

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Table 1: Oil Degrading Microbes in the Reactor at 8 Months

Location*	Total Heterotrophs/g	Oil Degraders/g
North top	8.6×10^7	4.6×10^7
Centre top	8.6×10^8	1.86×10^8
South top	4.6×10^8	8.6×10^7
North bottom	3.0×10^8	4.2×10^8
Centre bottom	1.86×10^9	8.6×10^8
South bottom	3.0×10^8	4.6×10^8
Sump	1.86×10^7	4.6×10^6

* Samples were taken from the top 30 centimeters and the bottom 30 centimeters of the reactor in a North/South alignment.

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Table 2: Water Analyses

COMPONENT	CONCENTRATION (microgram/L)*
Naphthalene	<2
Acenaphthylene	<2
Acenaphthene	<2
Fluorene	<2
Phenanthrene	<2
Anthracene	<2
Fluoranthene	<2
Pyrene	<2
Benzo(a)anthracene	<2
Chrysene	<2
Benzo(b)fluoranthene	<2
Benzo(k)fluoranthene	<2
Benzo(a)pyrene	<2
Indeno(1,2,3-cd)pyrene	<2
Dibenzo(a,h)anthracene	<2
Benzo(g,h,i)perylene	<2

* A detection limit of 2 microgram/L was used based on a water sample of 500 mL.

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Table 3: Oil Loss in the Reactor

SAMPLING TIME	OIL RECOVERED			
	Oil + Solids	Oil	% Oil	% Oil loss
Start	18.4	5.2	28.4	0
4 Weeks	22.6	6.4	28.4	0
8 Weeks	18.11	4.6	25.4	10.5
8 Months	25.1	1.8	7.2*	75
11 Months	35.4	2.6	7.3**	74

* The average of the oil content of six locations in the bioreactor; three from the top 30 cm and three from the bottom 30 cm. Oil contents were 7.7%, 5.5% and 6.0% in the top and 6.7%, 9.6% and 8.1% in the bottom in a north to south direction respectively.

** The oil content of a composite sample prepared by the Prince George refinery personnel.

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9.0 FIGURES

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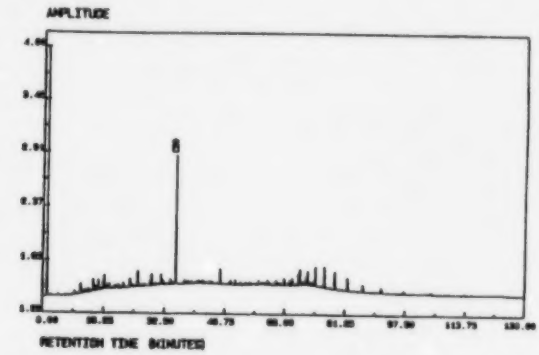
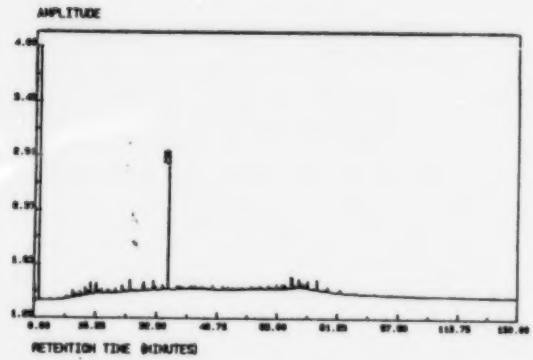
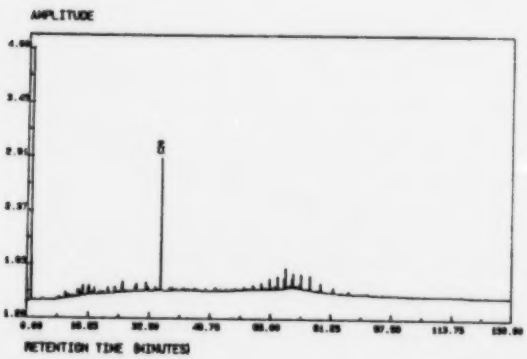
FIGURE 1. **GC PATTERNS OF THE OIL RECOVERED FROM 3 LOCATIONS AT THE TOP OF THE BIOREACTOR AFTER 8 MONTHS OPERATION (PANELS 1,2,3) COMPARED WITH THE OIL RECOVERED AT 8 WEEKS (PANEL 4). AT 8 MONTHS MOST OF THE ALKANES HAVE BEEN LOST.**



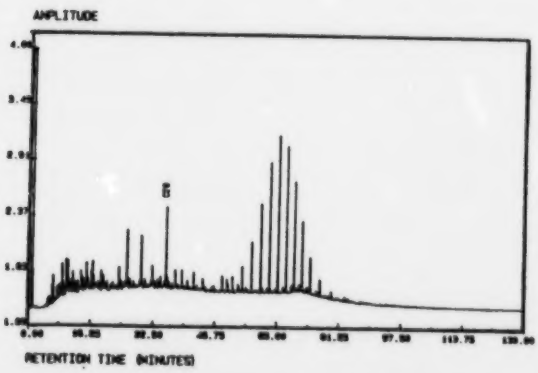
Panel 1
NORTH



Panel 2
CENTRE



Panel 3
SOUTH



Panel 4
EIGHT WEEKS

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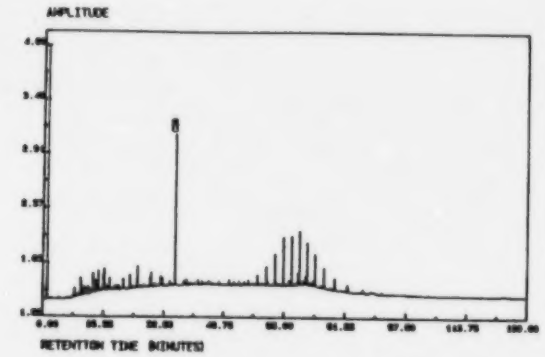
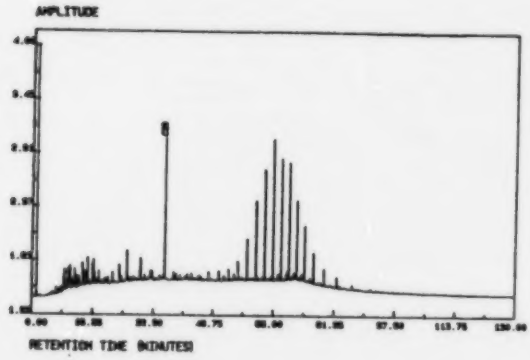
FIGURE 2: **GC PATTERNS OF THE OIL RECOVERED FROM 3 LOCATIONS AT THE BOTTOM OF THE BIOREACTOR AFTER 8 MONTHS OPERATION (PANELS 1,2,3) COMPARED WITH OIL RECOVERED FROM THE REACTOR AT 8 WEEKS (PANEL 4). THERE WAS LESS ALKANE LOSS AT THE BOTTOM OF THE REACTOR.**



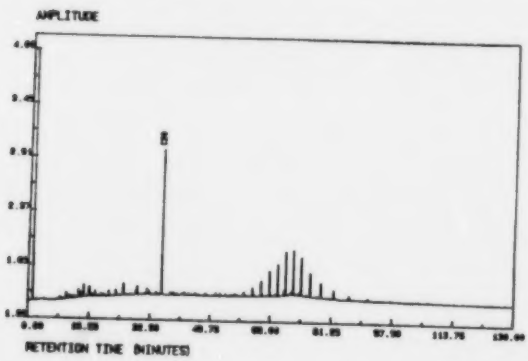
Panel 1

NORTH



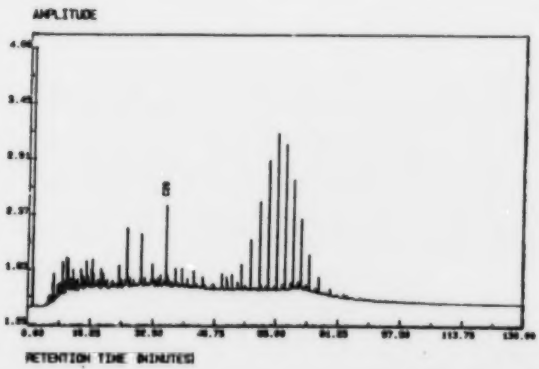
Panel 2

CENTRE



Panel 3

SOUTH



Panel 4

EIGHT WEEKS

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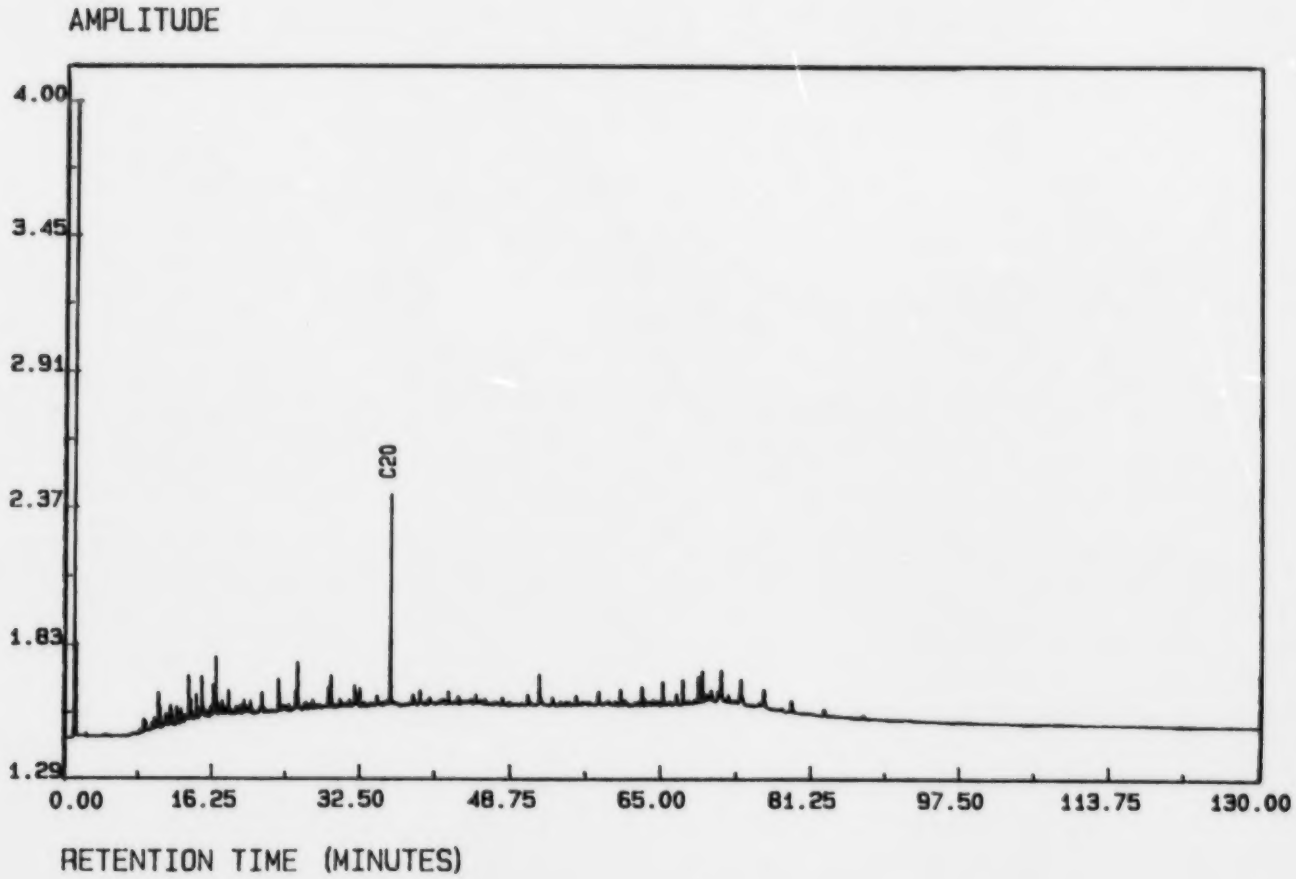
FIGURE 3: **GC PATTERNS OF THE OIL IN A COMPOSITE SAMPLE RECOVERED FROM THE BIOREACTOR AFTER 11 MONTHS OPERATION.**



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10.0 APPENDICES

APPENDIX I

DEAN STARK OIL EXTRACTION

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SYNCRUDE
ANALYTICAL METHODS FOR OIL SAND
AND
BITUMEN PROCESSING

SYNCRUDE CANADA LIMITED
EDMONTON, ALBERTA, CANADA
August 1979

Determination of Bitumen, Water and Solids Content of Middlings and Tailings Samples (Classical)

Scope: This method determines the bitumen, water and solids content of middlings and tailings samples. Preferred sample sizes range from 250 to 600 g, although the method may be modified for smaller samples.

Summary: The sample is separated into bitumen, water and solids by refluxing with toluene in a solids extraction apparatus. Condensed solvent and co-distilled water are continuously separated in a trap. The water is drained from the lower portion of the trap while the solvent recycles through the extraction thimble to dissolve bitumen. When the extraction is complete, the clean solids retained in the thimble are dried and weighed. A density measurement is employed to determine the bitumen content of the extract. Water is determined by difference.

Safety Considerations:

1. Hydrochloric acid — highly toxic by inhalation. A strong irritant to eyes and skin.
2. Toluene — moderately toxic by inhalation and skin absorption. Possesses irritant and anesthetic properties. Highly flammable.

Apparatus, Reagents, Materials:

1. Condenser — an indented tube condenser having a water jacket at least 535 mm long with a 29/42 standard taper male joint at the base.
2. Water trap — constructed to continuously separate water and solvent. The trap portion, which is approximately 25 mm in diameter and 220 mm long, has a volume of about 130 mL. The lower end is fitted with a stopcock for removal of water while the upper section has a 29/42 standard taper female joint to accommodate the condenser. The downcomer has a 103/60 standard taper male joint for connection to the kettle and is perforated with 3 mm diameter holes below the ground glass.
3. Kettle — a heat-resistant glass vessel having a capacity of 2000 mL. The neck has a minimum length of 390 mm and includes a 103/60 standard taper female joint.
4. Extraction thimble — Whatman 85 x 200 mm cellulose thimble, single thickness.
5. Thimble basket — a corrosion-resistant basket to support the thimble. See Figure 1. Fabrication from 3 mm diameter nichrome wire using a silver solde bottom joint is suitable.
6. Solvent distributor — corrosion-resistant, as shown in Figure 2.
7. Heating mantle — 500 W, to accommodate 2000 mL kettle.

The assembled extraction apparatus is shown schematically in Figure 3. If sample are less than 100 g, then the extraction apparatus described in Method 2.7 is use with the exception that the lower end of the water trap is fitted with a drain cock Volumes employed in the following procedure are then gauged accordingly.

8. Kimwipes — Type 1300.
9. Supply of 800 mL beakers.
10. Volumetric flasks — 250 and 1000 mL, Class A.
11. Syringe — 5 mL, glass, Luer-Lok tip.
12. Disposable filter assemblies — Millipore Millex filters, 0.45 µm, 25 m diameter, catalogue no. SLHA 025 OS.
13. Densimeter — six place densimeter with constant temperature water bath temperature control to ±0.01°C. The water bath is operated at 20°C.
14. Balances:
    Top loading balance to ±0.01 g, 1200 g capacity.
    Analytical balance.

15. Drying oven — forced draft, set at 120°C.
16. Desiccator.
17. Reagents:
    Hydrochloric acid. A.C.S. reagent grade.
    Toluene, A.C.S. reagent grade.
18. Distilled water.

Procedure: Sample Handling

1. Insert 3 Kimwipes into each of a quantity of thimbles. Place the thimbles into 800 mL beakers and weigh to the nearest 0.01 g.
2. Clean the outer walls of the sample container and lid. Weigh to the nearest 0.1 g. Carefully add 0.5 mL of concentrated hydrochloric acid to the sample. Then add approximately 100 mL of toluene and stir until all the bitumen adhering to the wall of the sample container is dissolved.
3. Remove the Kimwipes from the thimble, insert the thimble into a thimble basket and mount the basket by its support into the neck of a kettle. Add approximately 900 mL of toluene to the kettle by pouring it through the thimble.
4. Restir the sample and while it is still in motion transfer to the thimble. Wash the container with toluene to remove all the bitumen. Add the washings to the thimble. Transfer the bulk of the remaining solids by scraping with a spatula. Finally, rinse and transfer remaining solids with distilled water. Clean and dry the container and lid with the Kimwipes and place them in the thimble. Weigh the container and lid.

Extraction

5. Assemble the extraction apparatus as shown in Figure 3, ensure all joints are vapour tight, and begin refluxing. Drain and discard water from the trap when it nears the trap overflow. The extraction is complete when the level of water in the trap is constant and solvent dripping from the thimble is clear. Terminate the extraction and allow the apparatus to cool.

Calibration of Densimeter

6. Prepare a series of standard solutions of middlings and tailings bitumen in toluene covering the range 0.3 - 12 g/250 mL. (a)
7. Filter the standards through a 0.45 µm filter and determine the density of the solutions to six places.
8. Prepare a calibration curve by plotting the density of the standards versus the bitumen concentration in grams of bitumen per 250 mL. Calculate the slope and intercept of the plot using a linear least square regression. Coefficients of determination better than 0.999 are expected. The calibration does not have to be repeated daily, but several points on the calibration curve should be checked periodically to confirm the calibration.

Bitumen Determination

9. Disassemble the extraction apparatus and pour the bitumen/toluene extract into a 1000 mL volumetric flask and dilute to volume with toluene. Filter several milliliters of the solution through a 0.45 µm filter and determine its density to six decimal places. Ensure that the measured density falls within the range of the calibration.

Solids Determination

10. Remove the thimble from the extraction apparatus, place it in its beaker and dry for 12 hours at 120°C. Cool and reweigh.

Calculations: The bitumen, water and solids contents of the sample are given by:

$$\% \text{ Bitumen} = \frac{B}{W} \times 100$$

$$\% \text{ Solids} = \frac{S}{W} \times 100$$

$$\% \text{ Water} = 100 - (\text{wt \% Bitumen} + \text{wt \% Solids})$$

where: W = weight of sample, g

S = weight of solids recovered in thimble, g

$$B = \frac{\text{Sample Density} - \text{Calibration Intercept}}{\text{Calibration Slope}} \times 4$$

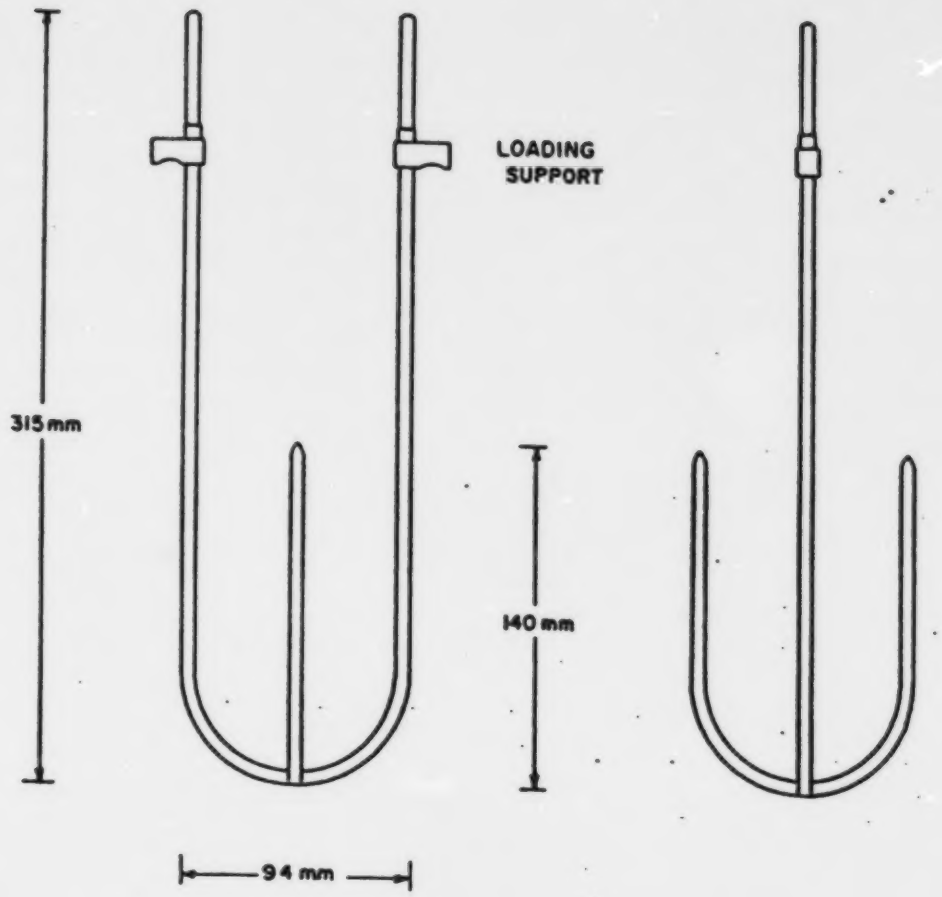
= weight of bitumen in sample, g

Precision: Data tabulated below indicates typical precision values associated with the bitumen water and solids analysis of middlings and tailings samples. Estimates reflecting th repeatability of a middlings analysis were determined on 37 replicate subsample prepared by Method 1.6 and analyzed using the small extractor assemblies. Precisic values for primary and secondary tailings were evaluated from 10 replicate sample obtained in rapid succession from pilot plant process streams and analyzed using larg extractor assemblies. All data includes errors due to sampling.

	Mean Value (wt%)	Standard Deviation (wt%)	Relative Standard Deviation
Middlings			
Bitumen	7.32	±0.15	2.05%
Water	75.91	±0.42	0.55%
Solids	16.77	±0.38	2.27%
Primary Tailings			
Bitumen	0.87	±0.06	6.90%
Water	35.01	±1.47	4.20%
Solids	64.12	±1.48	2.31%
Secondary Tailings			
Bitumen	0.44	±0.02	4.55%
Water	79.98	±1.71	2.14%
Solids	19.58	±1.71	8.73%

Comments:

a. The bitumen for the standard solutions is prepared by extracting a large numb of middlings and tailings samples on a solids extraction apparatus, removi non-filtered solids by centrifuging, removing toluene by evaporation, a determining the residual toluene content by the procedure described in Meth 2.7.



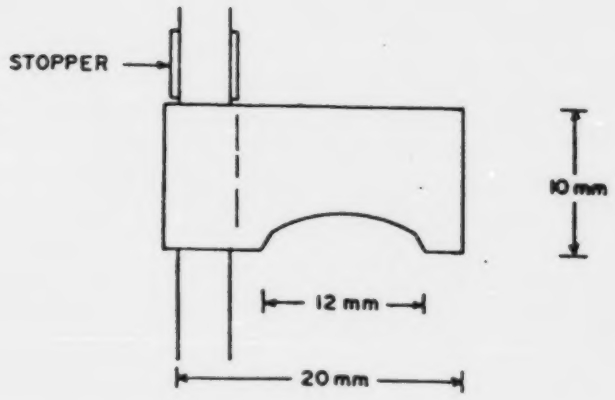


FIGURE 1: EXTRACTION THIMBLE BASKET

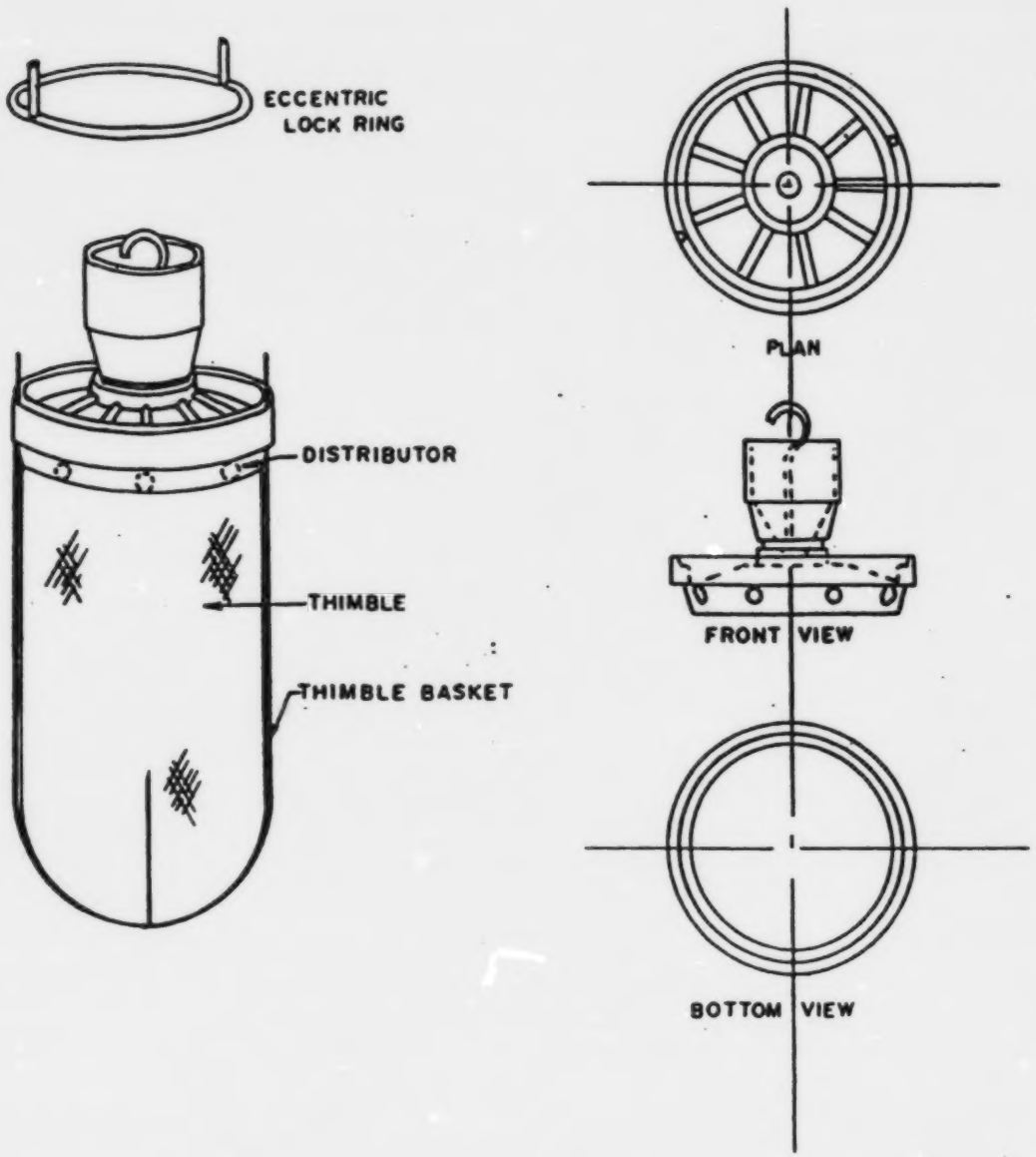


FIGURE 2: THIMBLE ASSEMBLY AND SOLVENT DISTRIBUTOR

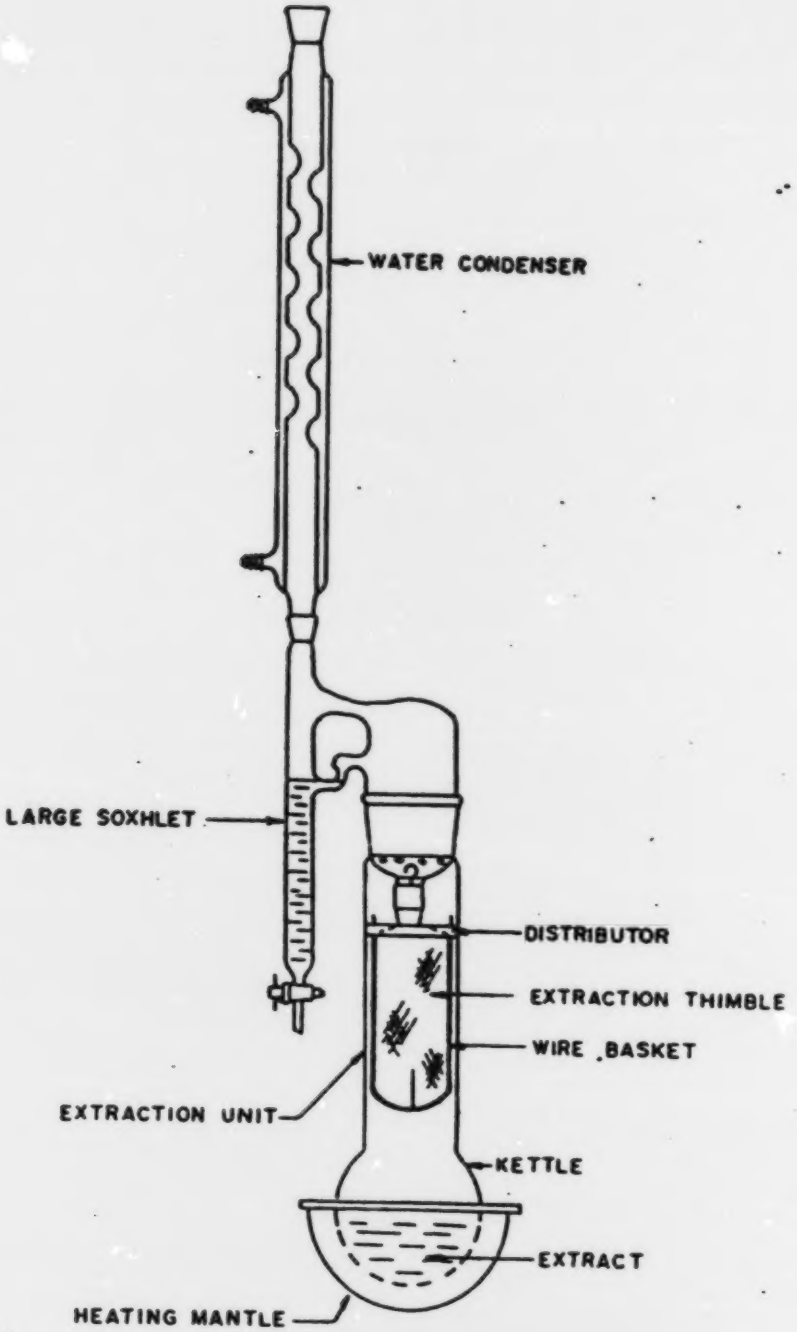


FIGURE 3: EXTRACTION APPARATUS

APPENDIX II

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

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ENVIRONMENTAL PROTECTION AGENCY

40 CFR Parts 261, 264, 265, 268, 271 and 302

[SWH-FRL-3782-2; EPA/OSW-FR-90-014]

RIN 2060-AA78

Hazardous Waste Management System; Identification and Listing of Hazardous Waste; Toxicity Characteristic Revisions

AGENCY: Environmental Protection Agency.

ACTION: Final rule; corrections.

SUMMARY: On March 29, 1990 (55 FR 11798), the Environmentl Protection Agency (EPA) promulgated a rule to revise the existing toxicity characteristics, which are used to identify those wastes which are hazardous and thus subject to regulation under subtitle C of the Resource Conservation and Recovery Act (RCRA) due to their potential to leach significant concentrations of specific toxic constituents. Since promulgation, the Agency has found the need to make corrections to the rule in order to ensure consistency of the toxicity characteristic leaching procedure (TCLP). Method 1311, with other methods contained in Test Methods for Evaluating Solid Waste (Physical/Chemical Methods), SW-846 and to clarify the section on quality assurance. This notice also corrects several errors in the March 29, 1990 notice.

DATES: Effective date: September 25, 1990. The effective date and compliance dates are not changed by this document.

FOR FURTHER INFORMATION CONTACT: For general information about this notice, contact the RCRA/Superfund Hotline at (800) 424-9346 (toll free) or (202) 382-3000 in the Washington, DC metropolitan area. For information on specific aspects of this notice, contact Steve Cochran, Office of Solid Waste (OS-332), U.S. Environmental Protection Agency, 401 M Street SW, Washington, DC 20460, (202) 475-8551.

I. SUPPLEMENTARY INFORMATION:

A. Background

On March 29, 1990 (55 FR 11798), EPA promulgated a rule to revise the existing toxicity characteristics, which are used to identify those wastes which are hazardous and thus subject to regulation under subtitle C of RCRA. The rule broadened and refined the scope of the hazardous waste regulatory program and fulfilled specific statutory mandates under the Hazardous and Solid Waste Amendments of 1984.

Today's notice makes corrections to appendix II of the regulatory language of the March 29, 1990 final rule, Method 1311, the TCLP. The method has been reorganized to correspond to the current version of Test Methods for Evaluating Solid Waste (Chemical/Physical Methods), SW-846. In addition, the quality assurance section has been renumbered and has been clarified to eliminate confusion. Today's notice also corrects several typographical errors and other omissions that appeared in the final rule revising the toxicity characteristics.

The preamble to the March 29, 1990 final rule stated that any person that would like to use the TCLP before the effective date of the rule (September 25, 1990) may do so in order to determine whether the eight heavy metals and six pesticides that are currently regulated under the Extraction Procedure (EP) Toxicity Characteristic leach at levels of regulatory concern. This language was included because the TCLP is required for both waste determination (on September 25, 1990, the TC effective date) and the land disposal restrictions program. The Agency today is clarifying that, while it is appropriate to use just one leach test to fulfill both requirements, persons that would like to continue using the EP leach test until the effective date of the TC rule may do so. It should be noted, however, that the EP test may still be required as a matter of state law, and this regulation does not affect such state law requirements.

B. Method 1311 and Quality Assurance

Today's notice makes technical corrections to mistakes made in Method 1311, and to errors made during typesetting, and provides clarifications to specific procedures of the method. The method also is being reorganized by placing the leaching procedure in one section and the quality assurance in a separate section to conform with the format used in SW-846.

A correction is being made in the calculation for the weight of waste to charge the Zero-Headspace Extractor (ZHE). In the final rule published March 29, 1990, the method incorrectly stated that the optimum sample size to charge into the ZHE should be determined for wastes containing >0.5% solids. This calculation results in a charge sample greater than the capacity of the ZHE. The Agency today is correcting the procedure to require a determination on wastes containing >5% solids. The sample holding times and errors made during typesetting are also being corrected by today's notice.

The Agency received inquiries indicating that confusion exists concerning correction factors and how they should be applied. Therefore, the Agency is making a technical correction in § 8.2.5 of Method 1311, published in today's notice, by adding a formula for correcting measured values for analytical bias. Also, inquiries indicate that EPA's discussion of the appropriate GC and GC/MS methods to be used was improper. The preamble language is corrected by today's notice to indicate the appropriate GC and GC/MS methods to be used.

Method 1311 is also being reorganized by today's notice by placing the leaching procedure itself in one section, 7.0. (The steps of the leaching procedure were previously presented in sections 7, 8, and 9 in the March 29, 1990 final rule.) In addition, this notice makes minor corrections to the quality assurance section and it is renumbered 8.0. This reorganization provides consistency with SW-846.

Appendix II, Method 1311 of the March 29, 1990 final rule is replaced in its entirety by Method 1311 of this notice in order to incorporate the corrections, reorganizations, and clarifications which are being made by today's notice.

The March 29, 1990 final rule provided an exclusion under 40 CFR 261.4 for petroleum-contaminated media and debris that fail the Toxicity Characteristic. This exclusion applies only to petroleum-contaminated media and debris which exhibit the TC for any one or more of the newly identified organic constituents, and which are subject to corrective action under part 280. The regulatory language of this exclusion in the final rule is revised by today's notice to correctly reflect this application.

C. Corrections

1. On page 11798, column one, under "DATES," in the second line of the compliance dates paragraph, change "generators: September 25, 1990. Small:" to "generators and treatment, storage, and disposal facilities (TSDFs): September 25, 1990. Small".

2. On page 11804, Table II.2—Toxicity Characteristics Constitutents and Regulatory Levels, change the column heading "Constituent (mg/L)" to "Constituent".

3. On page 11804, Table II.2—Toxicity Characteristic Constituents and Regulatory Levels, line twenty, change "Heptachlor (and its hydroxide)" to "Heptachlor (and its epoxide)".

4. On page 11815, column three, Table C-1—Chronic Toxicity Reference Levels, lines nineteen and twenty, change "Heptachlor (and its hydroxide)" to "Heptachlor (and its epoxide)".

5. On page 11825, column one, fourth bullet, first line, change "The data extracted from RFSs" to "The data extracted from RFAs".

6. On page 11828, column one, the first full paragraph (lines twenty-four) through thirty-six) is replaced by the following: "The Agency agrees that the GC method (Method 8040) or the GC/MS method (Method 8270) for phenols and the GC/Electron Capture Detection (GC/ECD) for phenoxyacid herbicides (Method 8150) are more advantageous for the analysis of these analytes because the equipment is more readily available than the HPLC, despite the associated difficulties. HPLC methods for phenols and phenoxyacid herbicides are not included in the third edition of SW-846 because of a lack of validation data. The Agency will allow only the use of the previously mentioned GC and GC/MS methods (Methods 8040 or 8270) or their equivalents for phenols and Method 8150 for phenoxyacid herbicides until such time that the Agency proposes an HPLC method."

7. On page 11831, column two, paragraph b, seventh line, change "rule of 40 CFR 262.3(a)(2)(iv) or the" to "rule of 40 CFR 261.3(a)(2)(iv) or the".

8. On page 11835, column one, first and second line, change "July 25, 1985" to "July 15, 1985".

9. On page 11837, column one, third complete paragraph, thirteenth line, change "for TSDFs on February 5, 1987 (53 FR" to "for TSDFs on February 5, 1987 (52 FR".

10. On page 11840, column three, first bullet of second complete paragraph, first line, change "Solid waste that is a hazardous waste" to "Used oil that is a hazardous waste".

11. On page 11844, Table IV-1.—TC Constituent and Regulatory Levels Proposed June 13, 1986—Continued, fourth line, change the CASNO for D034 from "78-44-2" to "78-44-8".

12. On page 11846, Table IV-1.—TC Constituent and Regulatory Levels Proposed June 13, 1986—Continued, line twenty-one, change to read as follows: D043 . . . . 1,1,1,2-Tetrachloroethane . . . . 630-20-6. . . .10.0.

13. On page 11844, column two, Table IV-2.—Organic Constituents, fourth line, change the CASNO for D021 from "106-90-7" to "108-90-7".

14. On page 11844, column three, Table IV-2.—Organic Constituents-Continued, first line, change "D031 . . . . Heptachlor (and its hydroxide) . . . . 76-44-2" to "D031 . . . . Heptachlor (and its epoxide) . . . .76-44-8".

15. On page 11848, Table IV-3—Toxicity Characteristic Constituents and Regulatory Levels—Continued, tenth line, change "Heptachlor (and its hydroxide)" to "Heptachlor (and its epoxide)".

16. Also on page 11848, column two, third line, change "270 of chapter 40." to "270 of title 40.".

PART 261—[AMENDED]

§ 261.4 [Corrected]

17. On page 11862, column two, in § 261.4 paragraph (b)(10), is corrected to read as follows:

10. Petroleum-contaminated media and debris that fail the test for the Toxicity Characteristic of § 261.24 (Hazardous Waste Codes D018 through D043 only) and are subject to the corrective action regulations under part 280 of this chapter.

§ 261.24 [Corrected]

18. Also on page 11862, column three, in § 261.24 Table 1.—Maximum Concentration of Contaminants for the Toxicity Characteristic, lines twenty-eight and twenty-nine, change "Heptachlor (and its hydroxide)" to "Heptachlor (and its epoxide)".

PART 271—[AMENDED]

§ 271.1 [Corrected]

19. On page 11876, in § 271.1(j) Table 1—Regulations Implementing the Hazardous and Solid Waste Amendments of 1984, the Federal Register reference should be "55 FR 11798-11877".

PART 302—[AMENDED]

§ 302.4 [Corrected]

20. On page 11877, in § 302.4, Table 302.4, List of Hazardous Substances and Reportable Quantities, in the first column, make the following corrections:

A. In the ninth line, change "Heptachlor (and hydroxide) (D031)" to "Heptachlor (and epoxide) (D031)."

B. In line twenty-five, change "Thrichloroethylene (D040)" to "Trichloroethylene (D040)".

C. In line twenty-six, change "2,4,5-Trichlorethylene (D041)" to "2,4,5-Trichlorophenol (D041)".

Dated: June 22, 1990.

Mary A. Gade,

Acting Assistant Administrator.

In addition to the corrections made above, part 261 is amended by revising appendix II to read as follows:

Appendix II—Method 1311 Toxicity Characteristic Leaching Procedure (TCLP)

1.0 Scope and Application

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte equals or exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 Summary of Method

2.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 µm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 µm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 Interferences

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 Apparatus and Materials

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ±2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels.

4.2.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of

volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see section 4.3.1). The vessels shall have an internal volume of 500–600 mL, and be equipped to accommodate a 90–110 mm filter. The devices contain VITON®[1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 pounds per square inch (psi) or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedures (see section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see section 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device [illegible] liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

Note: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see section 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 μm, or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Prefilters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1 L per rinse is recommended). Glass fiber filter are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25°C.

4.6 TEDLAR® bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., <1% of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., >1% of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100% solid) or has no significant solid phase (is 100% liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g. a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (see section 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or erlenmeyer flask.

4.11 Magnetic stirrer.

5.0 Reagents

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. Reagent water is defined as water in which an interferant is not observed at or above the methods detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.2.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing [illegible] (0.1 per

5.2.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.2.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 + 5 degrees C, bubble a contaminant-free inert gas (e.g., nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-

[1] VITON® is a registered trademark of DuPont.

[2] TEDLAR® is a registered trademark of Dupont.

headspace and seal with a Teflon-lined septum and cap.

5.3 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.4 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.5 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.6 Glacial acetic acid, CH_3CH_2OOH, ACS reagent grade.

5.7 Extraction fluid.

5.7.1 Extraction fluid #1: Add 5.7 mL glacial CH_3CH_2OOH to 500 mL of reagent water (See section 5.2), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05.

5.7.2 Extraction fluid #2: Dilute 5.7 mL glacial CH_3CH_2OOH with reagent water (See section 5.2) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05.

Note: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.8 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 The TCLP may place requirements on the minimal size of the field sample, depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more samples just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C. Samples should be opened only immediately prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see section 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See section 8.0 (QA requirements) for acceptable sample and extract holding times.

7.0 Procedure

7.1 Preliminary Evaluations. Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) Determination of the percent solids (section 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (section 7.1.2); (3) determination of whether the solid portion of the waste requires particle size reduction (section 7.1.3); and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste (section 7.1.4.).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in section 4.3.2 and is outlined in sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

Note: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in section 7.1.1.5 to determine he weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1–10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

Note: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Note: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in section 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (section 7.1.1.9)}}{\text{Total weight of waste (section 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to section 7.1.3 to determine whether the solid material requires particle size reduction or to section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in section 7.1.1.8 is less than 0.5%, then proceed to section 7.2.9 if the nonvolatile TCLP is to be performed and to section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100± 20°C until two successive weighings yield the same value within ± 1%. Record the final weight.

Note: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\% \text{ dry solids} = \frac{(\text{Weight of dry waste + filter}) - \text{tared weight of filter}}{\text{initial weight of waste (section 7.1.1.8 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to section 7.2.9 if the nonvolatile TCLP is to be performed, and to section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (section 7.1.3) and determine the appropriate extraction fluid (section 7.1.4). If only the volatile TCLP is to be performed, see the note in section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see section 7.3.6).

Note: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (section 7.2), determine the appropriate fluid (section 8.7) for the nonvolatiles extraction as follows:

Note: TCLP extraction for volatile constituents uses only extraction fluid #1 (section 8.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to section 7.3.

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to section 7.2.

7.1.4.3 If the pH from section 7.1.4.2 is >5.0, add 3.5 mL 1N NCL slurry briefly, cover with a watchglass, heat to 50°C, and hold at 50°C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (sections 7.1.1–7.1.4) was determined to be 100% solid at section 7.1.1.1, then it can be used for the section 7.2 extraction (assuming at least 100 grams remain), and the section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in section 7.3. The aliquot of the waste subjected to the procedure in section 7.1.1.7 might be appropriate for use for the section 7.2 extraction if an adequate amount of solid (as determined by section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved. A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in section 4.3.2 and is outlined in sections 7.2.3 to 7.2.6.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid-wash the filter if evaluating the mobility of metals (see section 4.4).

Note: Acid-washed filters may be used for all nonvolatile extractions even when metals are not of concern.

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids (sections 7.1.1 or 7.1.2), use the percent solids information obtained in section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Note: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of

this residue and subtract it from the sample weight determined in section 7.2.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1–10 psi, until air or pressurizing gas moves through the filter. If this point is reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

Note: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See section 7.2.12) or stored at 4°C until time of analysis.

Note: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.2.9 If the waste contains <0.5% dry solids (see section 7.1.2), proceed to section 7.2.13. If the waste contains >0.5% dry solids (see section 7.1.1 or 7.1.2), and if particle size reduction of the solid was needed in section 7.1.3, proceed to section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

Note: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (section 7.1.1)} \times \text{weight of waste filtered (section 7.2.5 or 7.2.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see section 7.1.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2°C during the extraction period.

Note: As agitation continues, pressure may build within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

7.2.12 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in section 7.2.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see section 4.6) if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from section 7.2.12 is defined as the TCLP extract. Proceed to section 7.2.14.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from section 7.2.12 with the initial liquid phase of the waste obtained in section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from section 7.2.7, is not or may not be compatible with the filtered liquid resulting from section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phase (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to section 8.0 for quality assurance requirements.

7.3 Procedure When Volatiles are Involved. Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500 mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4°C) to minimize loss of volatiles.

7.3.1 Pre-weigh the (evacuated) filtrate collection container (See section 4.8) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag.

whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in section 4.8 are recommended for use under the conditions stated in sections 4.8.1–4.8.3.

7.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from section 7.3, section 7.1.1 and/or 7.1.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

7.3.3 If the waste is 100% solid (see section 7.1.1), weigh out a subsample [25 gram maximum] of the waste, record weight, and proceed to section 7.3.8.

7.3.4 If the waste contains <5% dry solids (section 7.1.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing >5% dry solids (sections 7.1.1 and/or 7.1.2), use the percent solids information obtained in section 7.1.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

7.3.4.1 For wastes containing <5% solids (see Section 7.1.1), weigh out a 500 gram subsample of waste and record the weight.

7.3.4.2 For wastes containing >5% solids (see Section 7.1.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{percent solids (section 7.1.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

7.3.5 If particle size reduction of the solid portion of the waste was required in section 7.1.3, proceed to section 7.3.6. If particle size reduction was not required in section 7.1.3, proceed to section 7.3.7.

7.3.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle size as described in section 7.1.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4°C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

Note: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle size has been appropriately altered, proceed to section 7.3.7.

7.3.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

7.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

Note: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in section 7.3.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1–10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100% solid (see section 7.1.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to section 7.3.12.

7.3.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1–10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

Note: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.3.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

Note: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5% dry solids (see section 7.1.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to section 7.3.15.

7.3.11 The liquid phase may now be either analyzed immediately (See sections 7.3.13 through 7.3.15) or stored at 4°C under minimal headspace conditions until time of analysis.

Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (section 7.1.1)} \times \text{weight of waste filtered (section 7.3.4 or 7.3.8)}}{100}$$

7.3.12 The following sections detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See section 5.7).

7.3.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

7.3.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5–10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5–10 psi and check all ZHE fittings to ensure that they are closed.

7.3.12.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 22 ± 3°C during agitation.

7.3.13 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in section 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in section 7.3.9. All extract shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see sections 4.0 and 7.3.1).

Note: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

7.3.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from section 7.3.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from section 7.3.13 and the initial liquid phase (section 7.3.8) are collectively defined as the TCLP extract.

7.3.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analtye Concentration} = \frac{(V_1)(C_1)+(V_2)(C_2)}{V_1+V_2}$$

where:

V_1 = The volume of the first phases (L).
C_1 = The concentration of the analyte of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the analyte of concern in the second phase (mg/L).

7.3.16 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations. Refer to section 8.0 for quality assurance requirements.

8.0 Quality Assurance

8.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel.

8.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. The bias determined from the matrix spike determination shall be used to correct the measured values. (See sections 8.2.4 and 8.2.5.) As a minimum, follow the matrix spike addition guidance provided in each analytical method.

8.2.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

8.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP extract as that which was analyzed for the unspiked sample.

8.2.3 The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. Use of other internal calibration methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the analyte concentration of the TCLP extract when the recovery of the matrix spike is below the expected analytical method performance.

8.2.4 Matrix spike recoveries are calculated by the following formula:

$\%R$ (% Recovery) $= 100\ (X_s - X_u)/K$

where:

X_s = measured value for the spiked sample,
X_u = measured value for the unspiked sample, and
K = known value of the spike in the sample.

8.2.5 Measured values are corrected for analytical bias using the following formula:

$X_c = 100\ (X_s/\%R)$

where:

X_c = corrected value, and
X_s = measured value of the unspiked sample.

8.3 All quality control measures described in the appropriate analytical methods shall be followed.

8.4 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES (DAYS)

	From: Field collection to: TCLP extraction	From: TCLP extraction to: Preparative extraction	From: preparative extraction to: determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semivolatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable.

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

TABLE 1.—VOLATILE ANALYTES [1,2]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1,-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

[2] Benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene, trichloroethylene, and vinyl chloride are toxicity characteristic constituents.

TABLE 2.—SUITABLE ROTARY AGITATION APPARATUS [1]

Company	Location	Model No.
Analytical Testing and Consulting Services, Inc.	Warrington, PA, (215) 343-4490.	4-vessel (DC20S), 8-vessel (DC30), 12-vessel (DC20B).
Associated Design and Manufacturing Company.	Alexandria VA, (703) 549-9999.	2-vessel (3740-2), 4-vessel (3740-4), 8-vessel (3740-6), 8-vessel (3740-8), 12-vessel (3740-12), 84-vessel (3740-84).
Environmental Machine and Design, Inc.	Lynchburg, VA, (804) 845-8424.	8-vessel (08-00-00) 4-vessel (04-00-00).
IRA Machine Shop and Laboratory.	Santurce, PR, (809) 762-4004.	8-vessel (011001).
Lars Lande Manufacturing.	Whitmore Lake, MI, (313) 449-4116.	10-vessel (01VRE), 5-vessel (5VRE).
Millipore Corp.	Bedford, MA, (800) 225-3384.	4-ZHE or 4 1-liter, bottle extractor, (YT30ORAHW).

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

TABLE 3.—SUITABLE ZERO-HEADSPACE EXTRACTOR VESSELS [1]

Company	Location	Model No.
Analytical Testing & Consulting Services, Inc.	Warrington, PA, (215) 343-4490.	C102, Mechanical Pressure Device.
Associated Design and Manufacturing Company.	Alexandria VA, (703) 549-9999.	3745-ZHE, Gas Pressure Device.
Lars Lande Manufacturing [2].	Whitmore Lake, MI, (313) 449-4116.	ZHE-11, Gas Pressure Device.
Millipore Corporation.	Bedford, MA, (800) 225-3384.	YT30090HW, Gas Pressure Device.
Environmental Machine and Design, Inc.	Lynchburg, VA, (804) 845-8424.	VOLA-TOX1, Gas Pressure Device.

[1] Any device that meets the specifications listed in section 4.2.1. of the method is acceptable.

[2] This device uses a 110 mm filter.

TABLE 4.—SUITABLE FILTER HOLDERS [1]

Company	Location	Model/catalogue No.	Size
Nuclepore Corporation.	Pleasanton, CA, (800) 882-7711.	425910 410400	142mm, 47 mm.
Micro Filtration Systems.	Dublin, CA, (800) 334-7132, (415) 828-9010.	302400 311400	142 mm, 47 mm.
Millipore Corporation.	Bedford, MA, (800) 225-3384.	YT30142HW XX1004700	142 mm, 47 mm.

[1] Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic analytes are of concern. The 142 mm size filter holder is recommended.

TABLE 5.—SUITABLE FILTER MEDIA [1]

Company	Location	Model	Pore Size (μm)
Millipore Corporation.	Bedford, MA, (800) 225-3384.	AP40	0.7
Nuclepore Corporation.	Pleasanton, CA, (415) 463-2530.	211625	0.7
Whatman Laboratory Products, Inc.	Clifton, NJ, (201) 773-5800.	GFF	0.7
Micro Filtration Systems.	Dublin, CA, (800) 334-7132, (415) 828-9010.	GF75	0.7

[1] Any filter that meets the specifications in section 4.4 of the Method is suitable.

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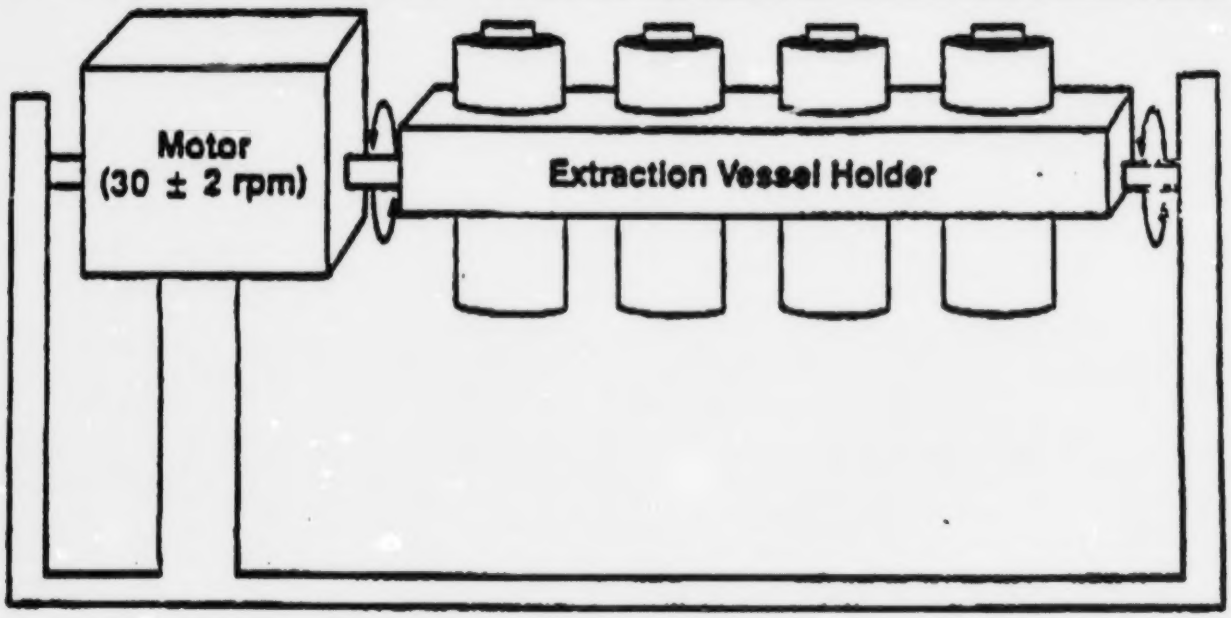


Figure 1. Rotary Agitation Apparatus

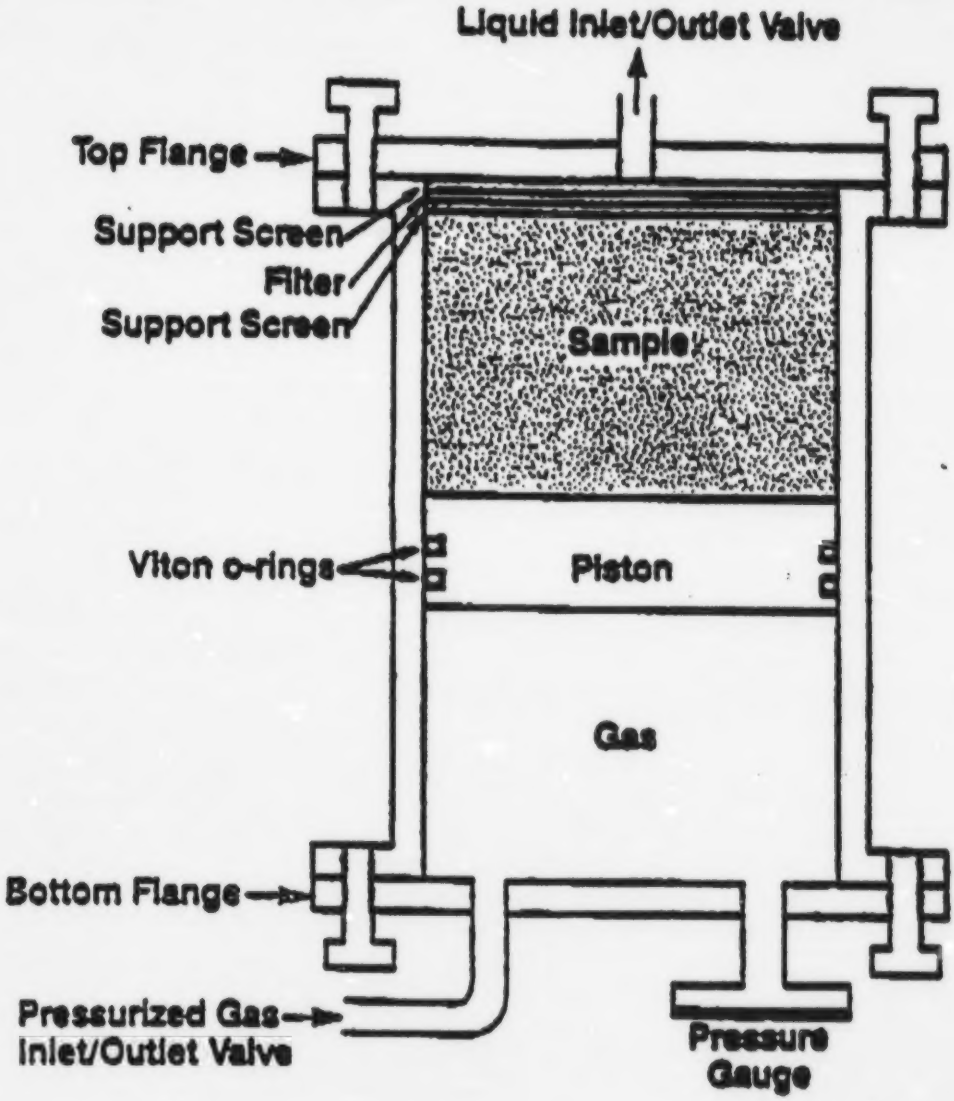
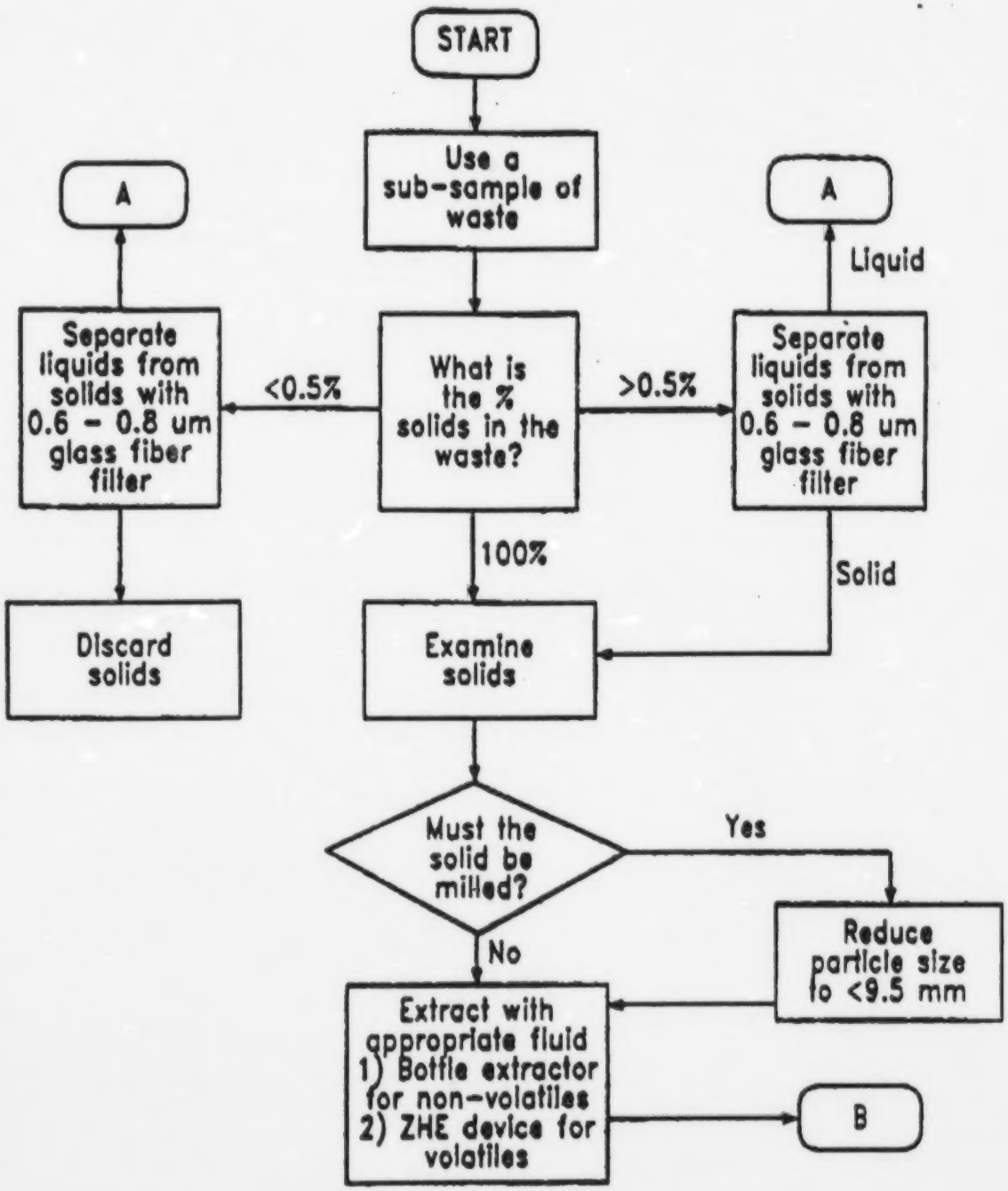


Figure 2. Zero-Headspace Extractor (ZHE)

METHOD 1311

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE


START
Use a sub-sample of waste
What is the % solids in the waste?
<0.5%
>0.5%
100%
Separate liquids from solids with 0.6 - 0.8 um glass fiber filter
Discard solids
A
Separate liquids from solids with 0.6 - 0.8 um glass fiber filter
Liquid
A
Solid
Examine solids
Must the solid be milled?
Yes
No
Reduce particle size to <9.5 mm
Extract with appropriate fluid 1) Bottle extractor for non-volatiles 2) ZHE device for volatiles
B

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METHOD 1311 (CONTINUED)

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE